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(54) Title: NO-COMPOUNDS FOR PSEUDO-LIVING RADICAL POLYMERIZATION
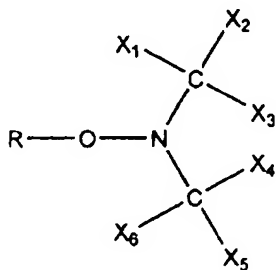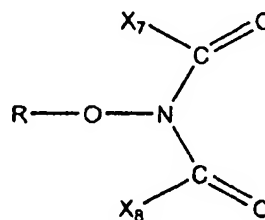
(57) Abstract

The invention pertains to a process for pseudo–living radical polymerization's in which use is made of specific NO–compounds, called initers, according to formula (I) or (II) wherein: R represents a group which has at least one carbon atom and is such that the free radical R. is capable of initiating the free radical polymerization of unsaturated monomers; at most five of the groups represented by X_1–X_6 are the same or different straight–chain or branched substituted or unsubstituted alkyl groups, wherein two or more of the groups may be linked to form cyclic structures, or wherein $-CX_1X_2X_3$ and/or $-CX_4X_5X_6$ are phenyl, the complementary groups X_1–X_6 are functional groups, and, X_7 and X_8 are independently selected from alkyl, aryl, alkaryl, and aralkyl, while X_7 is optionally linked with X_8 to form bridged structures. The invention further relates to certain NO compounds, (block) (co)polymers, and to a recycling process for such polymers.

NO-COMPOUNDS FOR PSEUDO-LIVING RADICAL POLYMERIZATION

Background of the invention

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The present invention relates to the use of NO-compounds as initers in pseudo-living radical polymerization processes, as well as to the polymers formed in such processes and to certain novel NO-compounds.

10 Currently, numerous institutes are investigating so-called "pseudo-living polymerization" processes. Such polymerization processes allow the production of polymers with a very narrow molecular weight distribution as well as of specific block-copolymers. Living polymerization processes have long been known from ionic processes such as the anionic polymerization of

15 styrene. There is a great interest in (pseudo) living polymerizations using free radicals, because such polymerizations would not suffer from many of the problems associated with living ionic polymerizations, for instance the need to use reactants of very high purity to avoid poisoning the reactive centre.

20 The current state of the art for (pseudo-) living polymerization processes involving radicals typically requires the use of a "stable free radical agent" in combination with an initiator, as described, for instance, in the recently issued patents US 5,498,679, US 5,449,724, US 5,412,047, and US 5,312,871, as well as in patent applications WO 95/26987 and WO 94/11412. The stable free

25 radicals of choice are usually compounds possessing stable nitroxide radicals. However, the synthesis of such stable free radical agents, as described, for instance, in *Macromolecules* **1996**, 29, 3323-3325, is cumbersome, and the nitroxide radicals thus obtained are quite expensive. The initiator in such prior art processes is typically used in such a quantity that the ratio of free radical

30 agent to the amount of radicals generated by the initiator is not unity, see for example WO 94/11412, and many side reactions take place, leading to both

undesired side products and a reduced initiator efficiency. The reduced initiator efficiency is often counterbalanced by using an excess of this product, with all associated disadvantages.

5   As an improvement on these known pseudo living radical polymerization processes, US 4,581,429 describes how nitroxide stable free radical compounds can be reacted with azo-initiators or with unsaturated compounds in combination with an initiator. The resulting alkoxyamines can be used in what are called "controlled-growth free radical polymerization" reactions of a

10   "living" nature. This concept was further elaborated on in *Macromolecules* **1995**, 28, 8722-8728, and *Macromolecules* **1996**, 29, 5246-5254, where it is demonstrated "how the alkoxyamine structure determines the C-O bond strength and what is required for these species to be successful initiators of living radical polymerization." In the former article it is disclosed that electron

15   donating or withdrawing groups - i.e., electron donating or withdrawing as compared with alkyl groups - on the nitroxide are undesired since they are "unlikely to be useful in living polymerization." Evaluation of the disclosed alkoxyamine compounds showed that they do not perform to full satisfaction in the polymerization. More particularly, both the polymer yield and control of the

20   molecular weight of this polymer needed improvement. Also, not all desired monomers could be polymerized in a controlled way.

The present invention relates to processes and NO-compounds which serve to avoid or minimize the disadvantages as reported for current polymerization

25   processes and existing NO-compounds.

Accordingly, it is the primary object of this invention to provide a pseudo-living polymerization process in which specific NO-compounds are combined with one or more of various monomers with subsequent polymerization at a variety

30   of temperatures.

It is another object of the invention to provide an economical polymerization process in which no additional initiators are used and no chain transfer agent or other means is required to produce polymers with a controlled molecular weight in high yields.

5

A third object of the invention is to provide an economical process to produce block copolymers using NO-compounds in pseudo-living polymerization processes. These copolymers can be, for instance, block, star, and/or comb copolymers.

10

A further object of the invention is to provide certain NO-compounds that can be used as initers in pseudo-living polymerization processes in which a variety of monomers can be polymerized in high yields, with accurate control of the molecular weight of the formed polymer, at various temperatures, which NO-

15   compounds are easy to synthesize.

Still another object of the invention is to provide a polymer that can easily be recycled to its monomeric compound(s) because of the NO end group of the polymer. This will make it possible for the polymers to be recycled at fairly low

20   temperatures without the addition of high-temperature initiators, thus allowing a more economical and environment-friendly recycling process.

These and other aspects of the invention are outlined in more detail below.

Description of the invention

As used herein, the term "pseudo-living polymerization process" stands for the radical polymerization process in which one or more ethylenically unsaturated
5   monomers are polymerized by means of at least one initer. According to a non-limiting theory, the polymerization kinetics in these novel processes depend, amongst others, on the thermal decomposition rate of the initer that is used. It is noted that the polymerization will not be of a perfect "living" nature. Also, it was observed that these polymerization kinetics are not necessarily the
10   same as conventional "pseudo-living" processes.

The term "initer" as used herein defines NO-compounds of a specific structure, as defined below. Such NO-compounds are referred to here as initers, for it is believed that the carbon-centred radical formed upon decomposition initiates
15   the polymerization, whereas the nitroxide radical will terminate the growing chain. Without the invention being limited to such a theory, it is further believed that the termination reaction is reversible at the polymerization temperature, so that monomers can be inserted between the last monomeric unit and the nitroxide moiety of the initer.

20

The first embodiment of the invention relates to a polymerization process in which at least one NO-compound with at least one moiety according to formula (I) or (II),

I)   II)

25

wherein:

- R represents a group which has at least one carbon atom and is such that the free radical R• is capable of initiating the free radical polymerization of unsaturated monomers;

- at most five of the groups represented by X_1-X_6 are the same or different straight-chain or branched, substituted or unsubstituted (cyclo) alkyl groups, while two or more of the groups X_1-X_6 may be linked to form cyclic structures,

- the complementary groups X_1 through X_6 are functional groups selected from substituted or unsubstituted phenyl, cyano, ether, hydroxy, nitro, dialkoxyphosphonyl, and carbonyl containing groups, or, alternatively, -$CX_1X_2X_3$ and/or -$CX_4X_5X_6$ represent a phenyl group,

- X_7 and X_8 are independently selected from alkyl, aryl, alkaryl, and aralkyl, while X_7 is optionally linked with X_8 to form bridged structures, and

is combined with a monomer composition to be polymerized.

Preferred examples of carbonyl containing functional groups are ester, carboxyalkyl, aldehyde, anhydride, and ketoalkyl groups.

Although X_1-X_6 may be linked to form cyclic structures, they preferably are not so linked. Also, it is preferred that each of X_1-X_8 contains fewer than 30 carbon atoms. More preferably, each of X_1-X_8 contains fewer than 10 carbon atoms in order to produce initers with a low molecular weight. Most preferably, at most five of X_1-X_6 are independently selected from methyl, ethyl, propyl, isopropyl, butyl, sec.butyl, tert.butyl, and cyclohexyl. X_7 and X_8 are preferably linked. More preferably, X_7 and X_8 are part of one substituted or unsubstituted phenyl or naftyl group. Most preferably, X_7 and X_8 ar part of one phenyl group.

Furthermore, it is preferred that the process involves initers with a moiety of formulae I or II, with the functional group being selected from phenyl, cyano, dialkoxyphosphonyl, carboxyalkyl, and ester. More preferred is a process where the initer possesses a cyano, phenyl, ester or dialkoxyphosphonyl

group. Even more preferred, is a process where the initer possesses a cyano or phenyl group. Most preferred is a process with at least one initer with a cyano moiety. Preferably, these initers can be produced without toxic by-products being formed. In this respect, it is noted that initers derived from 2,2'-

5   azobis(isobutyronitril) are less favoured because the toxin tetramethylsuccinonitril is a known decomposition product of this material.

Non-limiting examples of functional groups of the initer further include methylether, ethylether, propylether, butylether, poly(alkylether), methylketone,

10   ethylketone, propylketone, isopropylketone, butylketone, isobutylketone, tert.butylketone, diethoxyphosphonyl, ethoxypropoxyphosphonyl, dipropoxy-phosphonyl, dibutoxyphosphonyl, diisobutoxyphosphonyl, -$C(O)OCH_3$, -$C(O)OC_2H_5$, and C_1-C_{20} carboxylic acid esters.

15   The R group may bear one or more of the $ONC(X_{1-3})C(X_{4-6})$ functions as long as each of the radicals R• formed upon scission of one or more of the R-O bonds is capable of initiating the free radical polymerization of an unsaturated monomer. Furthermore, in the first instance it is preferred that R is not of a polymeric nature, meaning that R preferably does not comprise more than

20   approximately 4 recurring units incorporated by radically polymerizing one or more unsaturated monomers. Preferably, R does not contain more than two of such recurring units. Most preferred are compounds wherein R equals $C(X_{1-3})$ or $C(X_{4-6})$. However, the polymer that results from the polymerization process can be reused as an initer according to the invention. Therefore, R is not

25   limited to a non-polymeric group.

The NO-compounds can be used at various temperatures, with the choice of the NO-compound depending on the desired polymerization temperature. In this respect it is noted that radical polymerization reactions of (meth)acrylic

30   monomers are typically conducted at lower temperatures than (co)polymerizations involving styrene monomer. For other, regularly used,

monomers suitable polymerization temperatures are also well-known. The NO-compound of choice has an acceptable decomposition rate at the desired polymerization temperature, which is generally between 50 and 180°C. From, for instance, *Macromolecules,* 1995, 28, 8722-8728, it is known that the use of

5   electron withdrawing functional groups will stabilize the R-O bond, whereas electron donating functional groups will labilize it. Given this information and the teaching of this document, the man skilled in the art will have no problem selecting suitable types and numbers of functional groups to obtain usable NO-compounds. Before conducting actual polymerization experiments, the

10   half-life of the NO-compound may be determined in one or more well-known ways.

The invention is not limited to the use of NO-compounds alone. Also encompassed is the combination of such an NO-compound with additives

15   catalyzing its decomposition.

Preferably, the process according to the invention results in polymers with a number average molecular weight (Mn) close to the theoretical value (Mth), calculated from [monomer]/[initer]*$M_{monomer}$. More particularly, it is preferred

20   that the Mn does not exceed the Mth by 15 times. Most preferred is a process wherein Mn is less than five times Mth.

The ethylenically unsaturated monomers that can be polymerized and/or copolymerized by means of the NO-compounds include: styrene, divinyl-

25   benzene, α-methylstyrene, chloromethylstyrene, acrylic acid, esters of acrylic acid, methacrylic acid, esters of methacrylic acid, maleic acid, maleic anhydride, esters of maleic acid, fumaric acid, esters of fumaric acid, acrylonitrile, vinylpyridine, isoprene, butadiene, trienes, styrene phosphonic acid, vinyl phosphonic acid, styrene phosphonic esters, vinyl phosphonic acid

30   esters, maleimides, citraconimides, itaconimides, and vinylacetate. Also derivatives of these monomers obtained, for instance, by substituting a

functional group for a proton, can be used. Examples of suitable functional groups are halogen, hydroxy, amino, methoxy, nitro, carboxy, and cyano, but the invention is not limited to these.

5   In a second embodiment, the invention relates to a process in which an initer according to formula (I) or (II) is combined with a monomer composition to produce (co)polymers with a controlled molecular weight in good yield, without that additional radical generating species or chain transfer agents, which are known from classic radical polymerization processes, are introduced in the

10   process. Examples of radical generating species include, organic peroxides, azo-initiators and UV-initiators. The use of one or more initers with at least one moiety according to formula (I) or (II) in polymerization processes obviates such radical generating species or chain transfer agents because they allow a very high polymerization rate while the degree of polymerization (the number

15   of polymerized monomer units in the final polymer) remains close to the calculated value of the molar ratio of monomer to initer. The dispersity of the molecular weight distribution of the polymer will typically not be close to unity as in living polymerizations, but may vary from, for instance, 1.4 to 2.7. This range is indicative only; especially when block copolymers are made by

20   sequentially adding monomers, higher dispersity values have been observed.

Should the molecular weight of the polymer and/or its dispersity become too high, for instance, when excessive thermal polymerization of one or more of the monomers takes place, then the initer may be combined with a stable free

25   radical agent. In such a case, the stable free radical agent preferably will have the same structure as the nitroxide radical that results from thermal decomposition of the NO compound according to the invention.

In a third embodiment, the invention relates to polymers which are obtainable

30   by the polymerization processes according to the invention and will have one alkoxyamine end group, said end group being of the structure

-ON(CX$_1$X$_2$X$_3$)CX$_4$X$_5$X$_6$ or -ON(C(O)X$_7$)C(O)X$_8$, wherein X$_1$-X$_8$ are defined as above. Consequently, these polymers are themselves initers according to the invention. Hence, they can be used in further pseudo-living polymerization reactions in order to make, for instance, block copolymers. Before being used in such a fashion, the polymers may first be collected, purified, and dried. Preferably, however, the fresh monomer or monomer mixture can be added directly to the reaction mixture when it contains the desired polymer, for example, when a desired conversion, for example 90 percent by weight (%w/w), of the first monomer or monomer mixture is attained. Depending upon the reaction kinetics of the monomers involved, the presence of two or more monomers at the same time may result in a monomer distribution within the growing polymer segment of a random or more regular (for instance, alternating) nature. In this way, it is possible to produce (block) copolymers of varying nature in an economical fashion. Since the (block) copolymer obtained in turn is an initer according to the invention, subsequent polymerization steps are possible. Preferably, however, the initers according to the invention are low-molecular weight materials. More preferably, such initers have fewer than four recurring monomer units, since such products are easier to handle. With the initers and the process according to the invention one can produce block copolymers with specifically designed block compositions and sequences, resulting in materials with specific properties. They may be used as, for example, compatibilizers, coupling agents, dispersing agents for filled thermoplastics and SiO$_2$ filled rubber, telechelic slip agents, impact modifiers, anti-static agents, sizing agents, emulsifiers/surfactants, pigment dispersants, lubricants, processing aids, thickeners, adhesives, oil additives, and/or additives for the preservation and hardening of wood.

In a further embodiment, the invention relates to specific NO-compounds containing at least one moiety of the formula (I) which are pre-eminently suited to be used in the polymerization process according to the invention, wherein:

- R represents a group which has at least one carbon atom and is such that the free radical R• is capable of initiating the free radical polymerization of unsaturated monomers;

- at most five of the groups represented by X_1 through X_6 are the same or different straight-chain or branched substituted or unsubstituted (cyclo) alkyl groups, while two or more of the groups may be linked to form cyclic structures,

- the complementary groups X_1 through X_6 are functional groups selected from substituted or unsubstituted phenyl, cyano, ether, dialkoxyphosphonyl and carbonyl containing groups, such as ester, anhydride, and keto groups, and

- R is not polymeric when $-N(CX_1X_2X_3)$ $CX_4X_5X_6$ is 2,5-dimethyl-2,5-diphenylpyrrolidin-1-,

with the proviso that the NO-compound is not tris-(2-cyano-2-propyl)-hydroxylamine, tris-(2-carboxyethyl-2-propyl) hydroxylamine, and/or tris-(2-carboxymethyl-2-propyl)hydroxylamine.

Incidentally, it is noted that certain specific alkoxyamines are known which are not mentioned in US 4,581,429. Gingras and Waters describe the preparation of tris-(2-cyano-2-propyl) hydroxylamine in *J. Chem. Soc.*, **1954**, 1920-1924. Tris-(2-carboxymethyl-2-propyl)hydroxylamine is synthesized as described by Boyd in *J. Chem. Soc.*, **1958**, 2056, and tris-(2-carboxyethyl-2-propyl) hydroxylamine is synthesized by Masui in *Tetrahedron*, **1965**, 21, 2831. Also, the polymers mentioned in *Macromolecules* **1996**, 29, 3323-3325 and *J.M.S.-Rev.Macromol.Chem.Phys*, **1994**, 34(2), 288-289 are accidental anticipations of some initers according to the invention.

Upon thermal decomposition, with the R-O bond being broken, the NO-compounds according to formula (I) will generate two radicals. The carbon centred R• radical can initiate a polymerization reaction. However, during such a polymerization the nitroxide radical will terminate the growing chain, forming

a new initer which in turn is thermally labile and may be involved in subsequent polymerization reactions. In this way a pseudo-living radical polymerization will take place in which monomeric units are inserted at the nitroxide terminated end of the polymer. Because of the nature of such a process, the polymer that

5   is formed will have a polydispersity (D) typically greater than unity (1.0), the dispersity observed in regular living polymerization reactions.

The compounds according to the invention can be produced in various conventional ways. It was surprisingly found that the reaction of carbon-

10   centred radicals and nitric oxide (NO), which has been known since 1954 (see, for instance, *J. Chem. Soc.*, **1954**, 1920-1924), results in a very economical route to effective initers. Reactants and reaction conditions are chosen such that during the synthesis at least one of the two carbon-centred radicals attached to the nitrogen atom will bear a functional group. This is most easily

15   achieved by selecting the proper concentration of one or more of the functional group bearing carbon-centred radical precursors. Preferably, the functional group bearing carbon-free radical is obtained by the decomposition of one or more appropriate azo, C-C or other initiators such as diacyl peroxides with a high decarboxylation rate. Depending on the use of the initer, it may be

20   preferable to react only one type of carbon-centred radical (containing a functional group) with the NO gas.

Alternatively, compounds according to the invention can be produced by the well-known reaction of a nitroso compound under influence of heat or with

25   carbon-centred radicals. Depending on the structure of the nitroso compound, the man skilled in the art will have no problem selecting a suitable carbon-centred radical generating species in order to arrive at compounds according to the invention. An example of such a process is the preparation of N-tert.-butoxy phthalimide (BuPI), according to formula (II), and of the structure

12
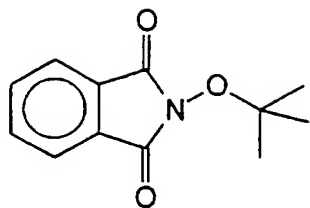
as described by T. Kolasa, A. Chimiak and A. Kitowski in *J. Prakt. Chem.*,
1975,317, 252-256.

5   The (block) (co)polymers that are made in the process of the present invention
     can fairly easily be recycled into low-molecular weight fragments. In contrast to
     current recycling processes as, for instance, known from European patent
     application EP-A-0273274 and non-prepublished European patent application
     96202111.9, filed on July 25, 1996, large amounts of compounds capable of
10   generating free radicals and very high temperatures are not needed. The low-
     molecular weight fragments that are formed can be used as a fuel. Hence, the
     (block) (co)polymers according to the invention can be recycled using less
     energy and without the use of specific additives. Preferably, the temperature in
     this recycling process is kept below 300°C.

15
     The invention will be further illustrated by the following examples.

Experimental

20   The chemicals used in the following examples were all reagent grade unless
     specified otherwise. Styrene and 1,2-dichlorobenzene (ODCB) were supplied
     by Baker (Baker PA grade). Styrene was freed of inhibitor by a treatment with
     an alkaline Al_2O_3 column. Methyl methacrylate (MMA), 2,2,6,6-tetramethyl-1-
     pyrrolidinyloxy (TEMPO®), and (+)camphorsulfonic acid (CSA), an agent
25   which is presumed to reduce thermal polymerization in pseudo-living radical
     polymerizations, were supplied by Aldrich. Perkadox® AIBN (2,2'-
     azobis[isobutyronitrile]), Perkadox® AMBN (2,2'-azobis[2-methylbutyronitrile]),

and all other initiators were supplied by Akzo Nobel or synthesized as laid down in the available documentation. NO gas was supplied by Indugas. Tinuvin® 123 is a product of Ciba Geigy.

5   Cumyl-TEMPO as used in the comparative examples was synthesized following the general procedure of EP 0 309 402, Example 63. More specifically, 0.454 mol of tert.butylhydroperoxide was dosed in five hours to a refluxing solution (atmospheric pressure) of 0.14 mol tetramethylpiperidine, 1.582 mol cumene, and 4 mmol MoO_3, and the mixture was reacted further at
10   this temperature for 12 hours. The reaction product was reacted with 0.17 mol of di-tert.butylperoxide in an autoclave at 140°C for four hours. Cumene was removed using a rotary evaporator, and cumyl-TEMPO was obtained by crystallization.

15   For polymerizations conducted in sealed tubes, the reaction mixture was degassed by means of well-known freeze-thaw techniques, after which the ampoule was sealed under vacuum. For polymerizations conducted in an open flask, a three-necked flask was fitted with a (gas) inlet, a stirrer, and a condenser. The contents of the flask were flushed with Argon before and
20   during the polymerization.

The conversion of monomer into polymer was determined in conventional ways by gas chromatographic (GC) analysis for monomer, using monochlorobenzene as the internal standard. Samples were taken by either
25   breaking an ampoule or through one of the necks of the flask, using a syringe. The reactants were quenched by rapid cooling and dissolved in dichloromethane (for GC analysis) or THF (for molecular weight analysis).

The number average molecular weight (Mn), weight average molecular weight
30   (Mw), and dispersity (D) of the polymers were analyzed in conventional ways

by means of size exclusion chromatography, using the THF solution as the eluent. Polystyrene samples were used as calibration standards.

Polymers were isolated from the solution by precipitation in n-pentane and subsequent drying in a vacuum oven at 50°C to constant weight (20-100

5   hours).

Polymers were characterized by means of 300 or 400MHz ^{1}H and 100 MHz ^{13}C NMR.

10 No attempt was made to optimize yields.

Example 1

Preparation of NO-compounds using NO gas

15

a) N,N,O-Tris-(1-cyano-1-methylethyl)hydroxylamine ((IBN)$_3$NO)
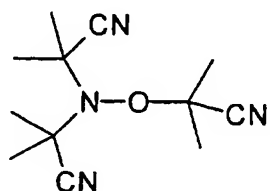
A solution of Perkadox AIBN (152.7 gr, 0.93 mol) in 1500 ml of toluene was

20 stirred, flushed with nitrogen gas, and heated to 76°C. A stream of nitrogen monoxide (5 l/hr) was passed through the solution, and a deep greenish/blue colour appeared. Heating was continued for 2 hours at 76°C, 1 hour at 82°C, 30 minutes at 88°C, 15 minutes at 94°C, and finally 15 minutes at 119°C to achieve complete decomposition of the AIBN. Residual nitrogen monoxide

25 was removed by flushing the reaction mixture with nitrogen gas, at which point the colouration changed to yellow. The solvent was removed at the rotary evaporator, and the resulting solution was steam-distilled to remove the by-

product tetramethyl succinonitrile. Next, the water/product mixture was left to cool down to room temperature, and the product precipitated. This solid was removed by filtration, dissolved in dichloromethane, and then dried with magnesium sulfate. Evaporation of the solvent gave 84.3 g (58%) of a yellow

5   solid, the (IBN)$_3$NO.

b) N,N,O-Tris-(1-cyano-1-methylpropyl)-hydroxylamine((MBN)$_3$NO)

10   A solution of Perkadox AMBN (178.8 gr, 0.93 mol) in 1500 ml of toluene was stirred, flushed with nitrogen gas, and heated to 76°C. A stream of nitrogen monoxide was passed through the solution, and a deep greenish/blue colour appeared. Heating was continued for 2 hours at 76°C, 1 hour at 82°C, 30 minutes at 88°C, 15 minutes at 94°C, and finally 15 minutes at 119°C to

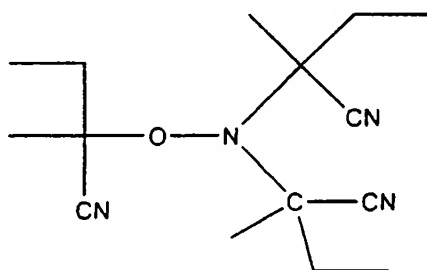15   achieve complete decomposition of the AMBN. Residual nitrogen monoxide was removed by flushing the reaction mixture with nitrogen gas, at which point the colouration changed to yellow. The solvent was removed using a rotary evaporator, and the resulting solution was steam-distilled in order to remove the by-product hexane-3,4-dinitrile. Next, the water/product mixture was left to

20   cool down to room temperature. The solution was extracted with ether, and the organic layer was dried with magnesium sulfate. Evaporation of the solvent gave 85.8 g (50%) of a yellow liquid, the (MBN)$_3$NO.

c) N,N,O-Tris-(1-cyano-1-cyclohexyl)hydroxylamine ((CCH)₃NO)
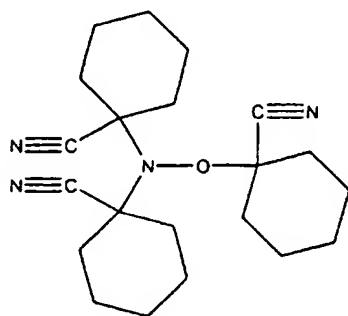
A solution of 30 g (0.123 mol) 1,1'-azobis(1-cyanocyclohexane) in 130 ml of
toluene was stirred, flushed with nitrogen gas, and heated to 76°C. A stream of
nitrogen monoxide (5 l/hr) was passed through the solution until a constant
blue colour appeared. Heating was continued for 2 hours at 100°C, 1 hour at
107°C, 30 minutes at 112°C, 15 minutes at 118°C, and finally 15 minutes at
125°C. Residual nitrogen monoxide was removed by flushing the reaction
mixture with nitrogen gas. The solvent was removed at the rotary evaporator,
and the resulting solution was steam-distilled to remove the by-product
di(cyclohexylnitrile). Next, the water/product mixture was left to cool down to
room temperature, and the product precipitated. This solid was removed by
filtration, dissolved in dichloromethane, and then dried with magnesium sulfate.
Evaporation of the solvent gave 15.3 g (53%) of an off-white powder, the
(CCH)₃NO.

17

Example 2

Preparation of NO-compounds involving nitroso compounds

<u>Bis-(2-cyano-2-propyl)-N-phenylhydroxylamine</u> ((IBN)$_2$ArNO)
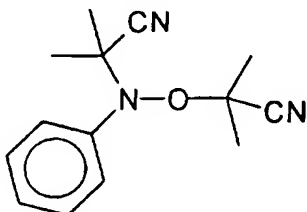
A suspension of Perkadox AIBN (65.6 gr, 0.4 mol) in 100 ml of toluene was added to a refluxing solution, at atmospheric pressure, of nitrosobenzene (21,4 g, 0.2 mol) in toluene (400 ml), with the aid of a Watson Marlow pump. The solution turned greenish/blue. AIBN was dosed during a period of 80 minutes. Heating was continued for 1 hour to complete decomposition of the AIBN. The solution became yellow. After steam-distillation, the residue was twice recrystallized in ether. 16 g (35%) of a yellow powder were obtained.

Example 3

Styrene, in a concentration of 4.1 mol/l in ODCB, was polymerized in a stirred
open flask under an argon atmosphere, at a temperature of 140°C for 6 hours.

5    $(IBN)_3NO$ was used in a concentration of 0.087 mol/l, and CSA was present in
a concentration of 0.027 mol/l. Samples were taken every 30 minutes.
Analyses of the samples gave following results:

Time (min)	Conversion (% w/w)	Mn (dalton)
0	0	
30	30.1	1430
60	45.9	2120
90	56.9	2550
120	65.7	2950
150	71.8	3100
180	76.7	3310
210	80.3	3400
240	83.1	3520
270	85.4	3530
300	86.7	3680
330	88.1	3670
360	89.3	3670

10   Extrapolation of the Mn to 100 % conversion results in values close to the
theoretical value for pseudo-living polymerizations, viz. 4200 vs. $[M]/[I]*M_{styrene}$
=4900. The deviation is believed to have been caused by some polymerization
of styrene monomer at the very beginning of the polymerization process. The
polymer was retrieved and characterization showed it to contain the expected
15   bis(2-cyano-2-propyl)-hydroxylamine groups.

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Comparative Example A

Styrene (bulk = 8.7 mol/l) was polymerized in a stirred open flask at 130°C under argon, using dibenzoyl peroxide (BPO) in a concentration of 0.072 mol/l
5   and 2,2,6,6-tetramethylpiperidinoxy free radical (TEMPO), with the following results.

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
0	0		
60	39	6090	1.33
120	44	7350	1.35
180	47	8430	1.37
240	65	12180	1.43
300	68	12810	1.43
360	82	15840	1.42

Also in this polymerization employing both a stable free radical agent and an
10   initiator, pseudo-living polymerization kinetics were observed. Also this polymer was analyzed after precipitation. The Tempo endgroups were clearly detectable together with the benzoyl end groups.

20

Examples 4-8 and Comparative Examples B-E

Pyrex tubes containing styrene, an NO-compound, and optionally CSA and/or
ODCB were degassed using a freeze-thaw method and sealed under vacuum.
5   The reaction mixture was polymerized at 140°C. The concentration of the NO-
compound was selected such as to give the indicated theoretical number
average molecular weight (Mth) at 100 % monomer conversion. In Examples 4
and 7 the styrene was mixed with ODCB in a 50/50 ratio (by weight). The
conversion and the molecular weight (distribution) of the polymer were
10   determined after 6 hours of reaction time, with the following results:

Exp.	Initer	CSA (mol/l)	Mth (Dalton)	Mn (Dalton)	Conversion (%w/w)	D
4	BuPI	0.027	4000	50300	30.1	n.d.
5	(IBN)$_2$ArNO	0.027	5000	30000	97.5	2.2
6	(IBN)$_3$NO	0.027	5000	4800	98.2	3.3
7	(MBN)$_3$NO	0.027	4000	3600	100.0	1.7
8	(CCH)$_3$NO	0.053	4300	3875	98.6	2.3
B	None	0	-	143400	90.9	2.4
C	None	0.027	-	173000	37.1	3.1
D	Cumyl-TEMPO	0.053	5000	119000	71.7	2.6
E	Tinuvin 123	0.053	1000	17000	n.d.	n.d.

n.d. = not determined

Clearly, the initer of choice has a pronounced effect on the molecular weight of
the polymer.

21

Examples 9-11 and Comparative Examples F-H

Example 4 was repeated using methyl methacrylate (MMA) (bulk = 9.3 mol/l) instead of styrene. Initers were selected and used in such a concentration as to give a polymer with Mth=5000, except in Example 11, where Mth=4000. CSA was used in a concentration of 0.027 mol/l in Examples G and 9-11. CSA was absent from Example F. In Example 11, the MMA was mixed with ODCB in a ratio of 50/50 (by weight). The following was observed after 6 hours of polymerization time.

Experiment	Initer	Mn (Dalton)	Conversion (%w/w)	D
9	(IBN)$_2$ArNO	13670	76.6	1.9
10	(IBN)$_3$NO	1892	79.4	2.6
11	(MBN)$_3$NO	3400	93.0	1.7
F	None	1106000	8.8	2.4
G	None	951250	6.6	2.1
H	Cumyl-TEMPO	205000	78.1	2.4

Again, the influence of the initers according to the invention on both the conversion rate and the molecular weight of the polymer is pronounced. Also, it was observed that using other TEMPO based initers did not allow control of the molecular weight.

Example 12

In sealed tubes, a solution of 4.4 mol/l of MMA in ODCB was polymerized at
140°C for 6 hours. (IBN)$_3$NO was used as initer at a concentration of 0.1 mol/l.
5   CSA was present in a concentration of 0.027 mol/l. The resulting polymer was
isolated and characterized with ^{1}H-NMR.

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
0	1.5	-	
45	84.3	2560	1.7
90	84.5	2545	1.7
135	84.4	2520	1.7
180	84.1	2550	1.7
225	84.6	2580	1.7
270	84.6	2565	1.7
315	84.3	2640	1.7
360	84.3	2615	1.7

The polymerization rates were exceptionally high. As in Examples 10 and 11,
10 a lower molecular weight than the theoretical value was observed. One of the
reasons for this may have been the fact that polystyrene standards were used
for calibration of the size exclusion chromatograph. NMR showed the expected
structure.

Example 13

In an open flask, a solution of 4.7 mol/l of MMA in ODCB was polymerized at 120°C for 6 hours. (IBN)$_3$NO in a concentration of 0.12 mol/l and CSA in a
concentration of 0.028mol/l were used. The final polymer was isolated and analyzed. The following results were obtained:

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
0	1.0	-	
15	55.7	3300	1.4
30	75.0	3335	1.4
45	81.1	3330	1.4
60	84.3	3260	1.4
75	86.2	3250	1.5
90	87.4	3190	1.5
105	88.0	3200	1.5
120	88.4	3240	1.5
240	89.9	3040	1.5
300	91.3	3030	1.5
360	91.3	3050	1.5

The results are comparable with the results from the previous example.

Examples 14-18 and Comparative Examples I and J

Example 4 was repeated using butyl acrylate (BA) instead of styrene and a polymerization temperature of 120°C. CSA was used in a concentration of 0.05 mol/l in all examples, except for Examples 14 and 16. The following was observed after 6 hours of polymerization time.

Experiment	Initer	Mth (Dalton)	Mn (Dalton)	Conversion (%w/w)	D
14	(IBN)$_3$NO	6432	6470	99.7	2.4
15	(IBN)$_3$NO	6184	6100	99.7	2.4
16	(MBN)$_3$NO	6066	5474	99.7	8.1
17	(MBN)$_3$NO	5926	5426	99.7	8.6
18	(IBN)$_2$ArNO	6531	53000	43.5	4.7
I	None	-	200000	44.6	2.8
J	Cumyl-TEMPO	5766	68900	16.6	2.2

These experiments show that butyl acrylate also can be polymerized efficiently.

Examples 19 and 20

In Examples 19 and 20, isoprene in ODCB (4.87 mol/l) was polymerized using 0.123 mol/l of $(IBN)_3NO$ and $(MBN)_3NO$, respectively (Mth=2700) in accordance with the procedure of Example 4, except that the polymerization temperature was 130°C. At some intervals, the content of a tube was analyzed, with the following results.

Example 19

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
60	26.3	4850	1.5
120	30.1	4850	1.6
180	36.3	4880	1.7
240	46.4	4930	1.7
300	52.1	4800	1.7
360	55.8	4860	1.7

Example 20

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
60	27.5	31200	1.5
120	38.1	3180	1.6
180	49.4	3330	1.7
240	59.2	3320	1.7
300	64.2	3470	1.7
360	68.6	3460	1.7

These experiments show that isoprene also can be polymerized efficiently.

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Examples 21-28

Using pyrex tubes, styrene (4.12 mol/l) in ODCB was polymerized for six hours
using 0.12 mol/l of $(IBN)_3NO$, (Mth = 3550) as described in Example 4, at a
5   temperature as specified in the following table. In Examples 21-24 no CSA
was used, while in Examples 25-28 the concentration of CSA was 0.027 mol/l.

Example	Temperature (°C)	Conversion (%)	Mn (Dalton)
21	80	<1	950
22	100	4.5	1050
23	120	41.2	3000
24	150	99.0	3390
25	80	<1	1000
26	100	4.6	970
27	120	36.3	2780
28	150	98.0	2280

10   Repeating these experiments with $(MBN)_3NO$ gave comparable results, except
that faster polymerization rates were observed.

Examples 29-31 and Comparative Example K

In these examples the performance of initers·in a polymerization to make high
solid acrylic resins was evaluated. To this end, using a stirred glass reactor
5   equipped with a condensor, a mixture consisting of 40 g butyl acrylate, 28 g
hydroxyethyl methacrylate, 20 g styrene, 10 g methyl methacrylate, 2 g maleic
anhydride, and 21.4 meq. initer or 30.0 meq. tert.butylperoxy 2-ethylhexanoate
(Trigonox® 21) (see table) was metered to 40 g solvent (see table), in a
nitrogen atmosphere at atmospheric pressure, in four hours. During the
10   addition the temperature of the reaction mixture was maintained at 126 or
140°C (see table). After the addition, the reaction mixture was further reacted
for one hour at the specified temperature. The following results were obtained
after analysis of the product.

15

Example	Radical source	reaction temp. (°C)	solvent	solids (%)	Mn (Dalton)	Disp
29	$(IBN)_3NO$	126	nBuAc	66.0	4100	1.9
30	$(IBN)_3NO$	140	S-100	70.0	3000	2.1
31	$(MBN)_3NO$	140	S-100	70.9	2700	2.1
K	Trigonox 21	140	S-100	70.8	3200	2.1

nBuAc = n-butylacetate

S-100 = Solvesso® 100

20   The initers according to the invention allow the production of a high solids resin
at various temperatures in good yields with a molecular weight that is lower
than observed in conventional processes.

28

Example 32

In an open flask, 3.3 mol/l styrene (18 g) in ODCB was polymerized at 140°C
for 6 hours, using 9 g of the product obtained in Example 3 as the initer and
5   0.027 mol/l CSA. The following results were obtained:

Time (min)	Conversion (%w/w)	Mn (Dalton)	D
0	0	-	
45	14.8	8620	2.0
90	30.2	10100	2.2
135	41.7	11050	2.2
180	51.3	12070	2.3
225	58.9	12830	2.2
270	65.4	13170	2.3
315	70.7	13530	2.3
360	74.6	13730	2.3

Characterization of the polymer showed the expected product to be formed.

Example 33

The previous example was repeated, except that the initer of Example 3 was replaced by the initer obtained in Example 13, with the following results.
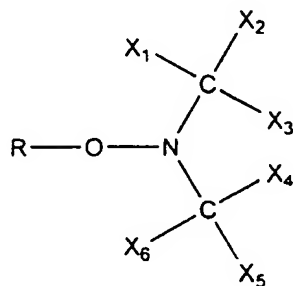
5

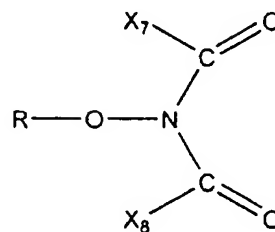| Time (min)	Conversion (%w/w)	Mn (Dalton)	D
0	1.2	3170	1.8
45	6.7	3590	2.1
90	12.7	4200	2.4
135	16.7	4650	2.5
180	21.3	5060	2.5
225	25.0	5320	2.6
270	27.4	5650	2.5
315	28.9	5930	2.5
360	31.2	6070	2.5

Again it was shown with 1H-NMR that the expected copolymer was formed.

30

Claims

1.   A pseudo-living polymerization process in which at least one NO-
      compound with at least one moiety according to formula (I) or (II),
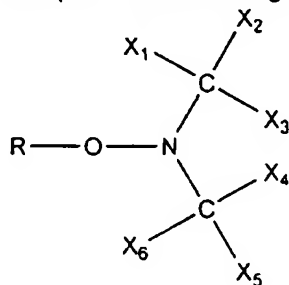

5

wherein:

- R represents a group which has at least one carbon atom and is
  such that the free radical R· is capable of initiating the free radical
10   polymerization of unsaturated monomers;
- at most five of the groups represented by X_1-X_6 are the same or
  different straight-chain or branched, substituted or unsubstituted
  (cyclo) alkyl groups, while two or more of the groups X_1-X_6 may be
  linked to form cyclic structures,
15   - the complementary groups X_1 through X_6 are functional groups
  selected from substituted or unsubstituted phenyl, cyano, ether,
  hydroxy, nitro, dialkoxyphosphonyl, and carbonyl containing groups,
  or, alternatively, $-CX_1X_2X_3$ and/or $-CX_4X_5X_6$ represent a phenyl
  group,
20   - X_7 and X_8 are independently selected from alkyl, aryl, alkaryl, and
  aralkyl, while X_7 is optionally linked with X_8 to form bridged
  structures, and
  is combined with a monomer composition to be polymerized.

25 2.   A process according to claim 1 wherein the complementary functional
      groups X_1-X_6 are phenyl or cyano.

3.   A process according to claim 1 or 2 wherein two or more ethylenically unsaturated monomers are polymerized, either sequentially or simultaneously.

5

4.   A process according to any one of the preceding claims, characterized in that the ethylenically unsaturated monomers are selected from styrene, divinylbenzene, α-methylstyrene, chloromethylstyrene, acrylic acid, esters of acrylic acid, methacrylic acid, esters of methacrylic acid,

10   maleic acid, maleic anhydride, esters of maleic acid, fumaric acid, esters of fumaric acid, acrylonitrile, vinylpyridine, isoprene, butadiene, trienes, styrene phosphonic acid, vinyl phosphonic acid, styrene phosphonic esters, vinyl phosphonic acid esters, maleimides, citraconimides, itaconimides, vinylacetate, their derivatives, and

15   substituted analogues.

5.   A process according to any any one of claims 1-4, characterized in that the reactants do not comprise free radical generating species other than one or more NO-compounds of formula I or II.

20

6.   A process according to any one of claims 1-5, characterized in that the molecular weight (distribution) of the resulting polymer is controlled by the concentration of monomer and NO-compound.

25   7.   A process according to any one of claims 1-6 wherein an additional stable free radical is used.

8.   A process according to claim 7 wherein the stable free radical is similar to the nitroxide radical that is formed when one or more of the applied

30   NO-compounds is thermally decomposed.

9.   A (block) (co)polymer obtainable by any one of the processes of claims 1-8.

10.   An NO-compound containing at least one moiety of the formula (I),

(I),

wherein:

- R represents a group which has at least one carbon atom and is such that the free radical R· is capable of initiating the free radical polymerization of unsaturated monomers;

- at most five of the groups represented by X_1 through X_6 are the same or different straight-chain or branched substituted or unsubstituted (cyclo) alkyl groups, while two or more of the groups may be linked to form cyclic structures,

- the complementary groups X_1 through X_6 are functional groups selected from substituted or unsubstituted phenyl, cyano, ether, hydroxy, nitro, dialkoxyphosphonyl, and carbonyl containing groups, such as ester, carboxyalkyl, aldehyde, anhydride, and ketoalk(ar)yl groups, and

- R is not polymeric when $-N(CX_1X_2X_3)\ CX_4X_5X_6$ is 2,5-dimethyl-2,5-diphenylpyrrolidin-1-,

with the proviso that the NO-compound is not tris-(2-cyano-2-propyl)-hydroxylamine, tris-(2-carboxyethyl-2-propyl)hydroxylamine, and/or tris-(2-carboxymethyl-2-propyl)hydroxylamine.

11.   An NO-compound according to claim 10, characterized in that the complementary groups X are selected from substituted or unsubstituted

phenyl, cyano, ether, and carbonyl containing groups, such as ester, anhydride, and ketoalk(ar)yl groups.

12.   A recycling process in which a polymer is converted into low-molecular weight fragments, characterized in that the polymer is obtained from a pseudo-living polymerization process according to any one of claims 1-8.

13.   A recycling process according to claim 12, characterized in that the processing temperature is below 300°C.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F4/00   C07C255/11   C07C255/46

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5 627 248 A (KOSTER ROBERT A ET AL) 6 May 1997 see compounds (18) - (21) see claims ---	1,10
X	EP 0 135 280 A (COMMW SCIENT IND RES ORG) 27 March 1985 see the whole document, in particular: see page 4, line 21 - page 9, line 14 see example 4 see claims 1,3-8,10-16	1-4,10, 11
Y	idem. --- -/--	1,10

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of theinternational search	Date of mailing of the international search report
10 February 1998	03/03/1998

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
Y	G. MOAD AND E. RIZZARDO: "Alkoxyamine-Initiated Living Radical Polymerisation" MACROMOLECULES, vol. 28, pages 8722-8728, XP002055156 cited in the application see the whole article, in particular schemes 1-3	1,10
Y	B.A. GINGRAS AND W.A.WATERS: "Properties and Reactions of Free Alkyl Radicals in Solution" JOURNAL OF THE CHEMICAL SOCIETY, 1954, pages 1920-1924, XP002050740 cited in the application	1,10
X	idem. see structures (III) and (IV), tables 1 and 3	10
X	A.N. BOYD, F.P. SOUTHERN, AND W.A. WATERS: "Properties and Reactions of Free Alkyl Radicals in Solution - part X" JOURNAL OF THE CHEMICAL SOCIETY, 1958, pages 2056-2058, XP002055157 cited in the application see compounds in the experimental section on page 2057	10

INTERNATIONAL SEARCH REPORT

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5627248 A	06-05-97	US	5677388 A	14-10-97
EP 0135280 A	27-03-85	AU	571240 B	14-04-88
		DE	3486145 A	17-06-93
		JP	1797643 C	28-10-93
		JP	5006537 B	26-01-93
		JP	60089452 A	20-05-85
		US	4581429 A	08-04-86
		AU	3037884 A	17-01-85